

# Understanding Structural Changes in LMR-NMC Materials

**Project ID: ES194**

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Voltage Fade Team

Annual Merit Review

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# Overview

## Timeline

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 75%

## Budget

- Voltage Fade project

## Barriers

Development of a PHEV and EV batteries that meet or exceed DOE/USABC goals.

## Partners

- ORNL
- NREL
- ARL
- JPL



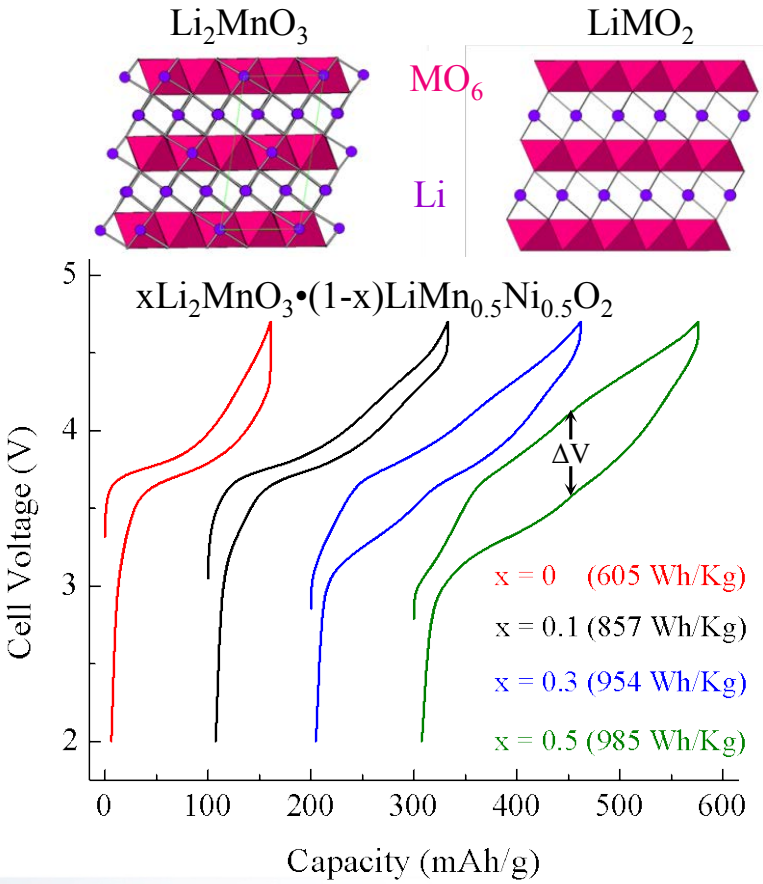
# Relevance

- Lithium- and manganese-rich (**LMR-NMC**) composite cathodes offer considerable gains over current state-of-the-art chemistries.
- Voltage fade** and **hysteresis** represent significant challenges to the commercialization of these oxides.
- An **atomic level understanding** of the mechanisms driving voltage fade and hysteresis is necessary for the design of novel, **robust LMR-NMC** cathodes.

Parameters of currently available Li-ion cathodes

Material	Voltage (vs. Li/Li <sup>+</sup> )	Capacity (mAh/g)	Sp. En. (Wh/Kg)
LiCoO <sub>2</sub>	3.8	150	570
LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub>	3.7	170	629
LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	3.7	185	685
LiMn <sub>2</sub> O <sub>4</sub>	4.0	110	440
LiFePO <sub>4</sub>	3.4	160	544

Composite cathode energy densities



# Approach

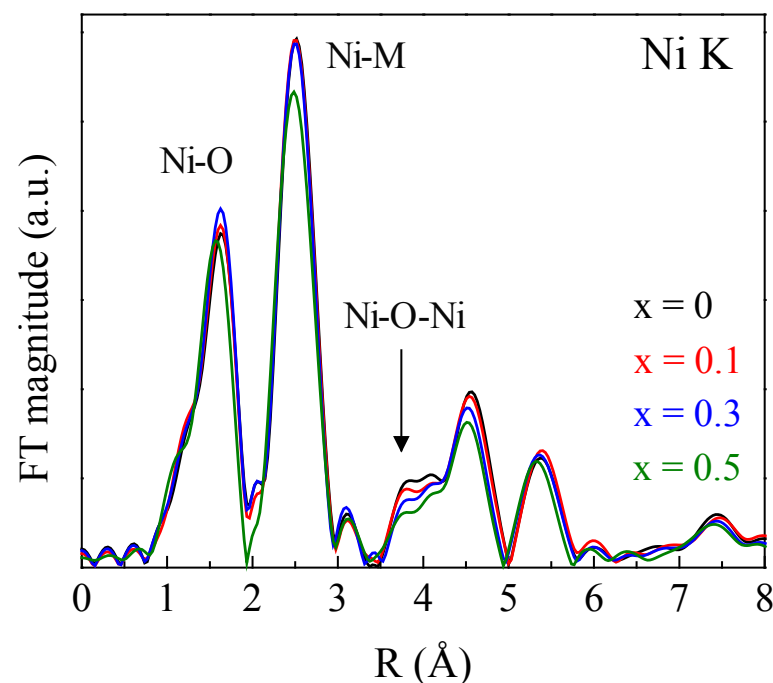
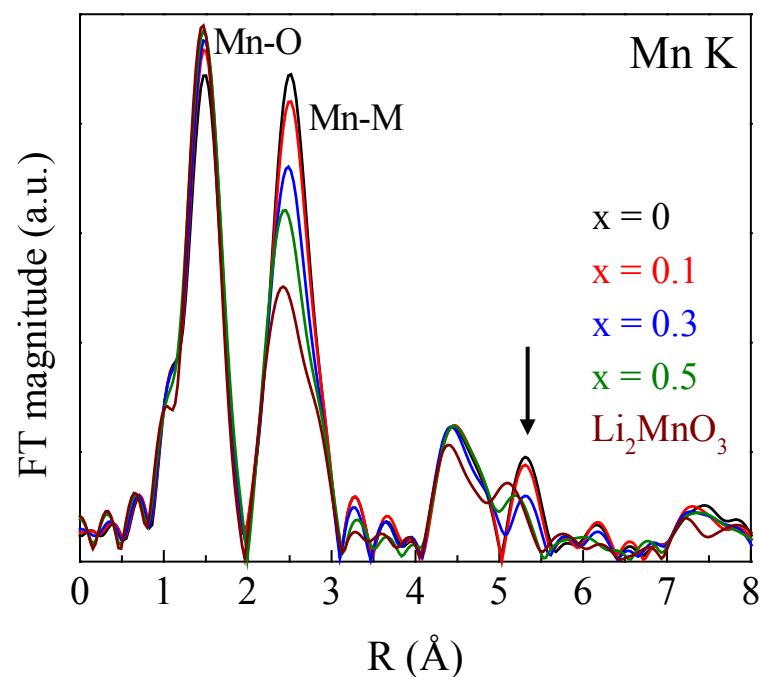
- Take advantage of DOE national user facilities to gain insights into the factors affecting voltage fade and hysteresis.
- Develop an atomic-level model that captures the essential electrochemical observations associated with voltage fade and hysteresis.
- Provide experimental data to the theory component of the voltage fade team to further evaluate the model.
- Provide feedback to the synthesis component of the voltage fade team.
- Design and carry out experiments to validate and refine our understanding of voltage fade and hysteresis.
- Use the understanding/information gained to aid the design of more robust cathode structures.



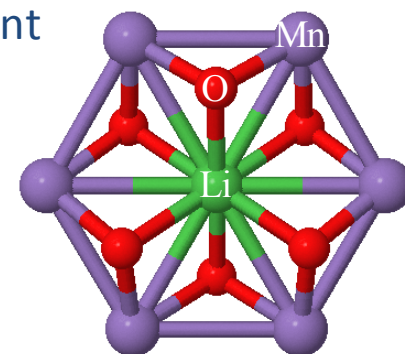
# Progress - What We Know About LMR-NMC

- **Local structure** is driven by charge ordering giving regions of two types:
  - TM-rich ( $\text{LiMO}_2$ ) – High M-M coordination giving “standard” electrochemical behavior.
  - Mn-rich ( $\text{Li}_2\text{MnO}_3$ ) – Li/Mn rich regions which show strong tendencies for Li-Mn ordering.  
Low Mn-M coordination, electrochemically different than bulk  $\text{Li}_2\text{MnO}_3$ .
- **Activation** of the “ $\text{Li}_2\text{MnO}_3$  component” ( $\text{LiMn}_6$ -type ordered regions) is necessary to induce **voltage fade** – concomitant with a **structural hysteresis**.
- Voltage fade and hysteresis increase with increasing Li and Mn ordering  
→ increasing x in  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ .
- Mn-rich regions undergo more severe structural changes relative to TM-rich regions → **Li/Mn ordering plays a key role in VF and hysteresis**.
- **Hysteresis and voltage fade are correlated** and depend on Li utilization, voltage, rate, and temperature (cycling is worse than high voltage ageing).
- A **model** has been developed to help us understand these observations.





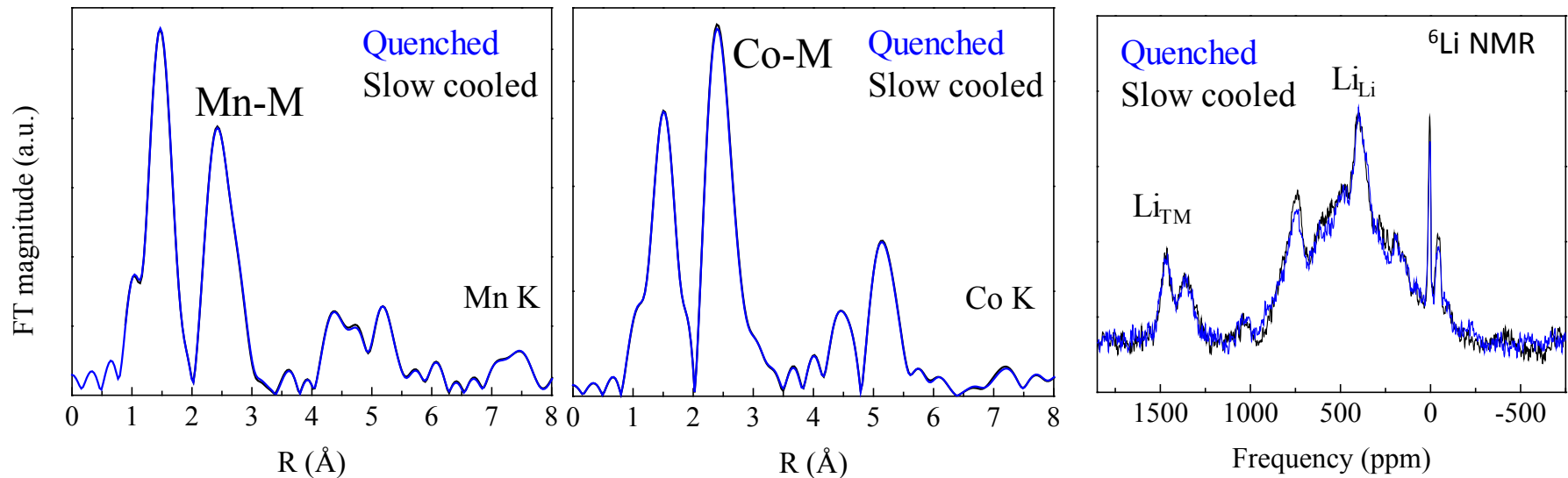
- Mn-M coordination decreases with increasing x. Local environment tends towards that of pure  $\text{Li}_2\text{MnO}_3$  (no peak at ~4 Å).
- Changes to local nickel environment are relatively small (peaks at ~4 Å).
- Charge ordering** is a dominating factor dictating **local structure**. Most Li/Ni exchange associated with MnNi-rich component (Ni-O-Ni).



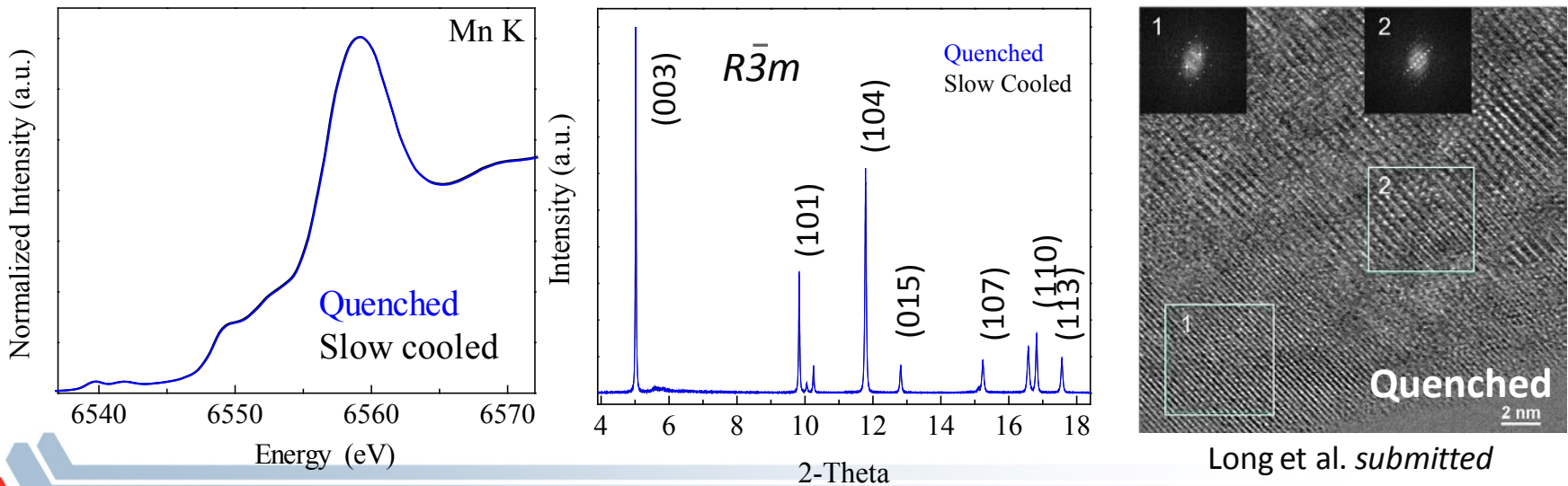
# Synthesis and Control Over Local Ordering

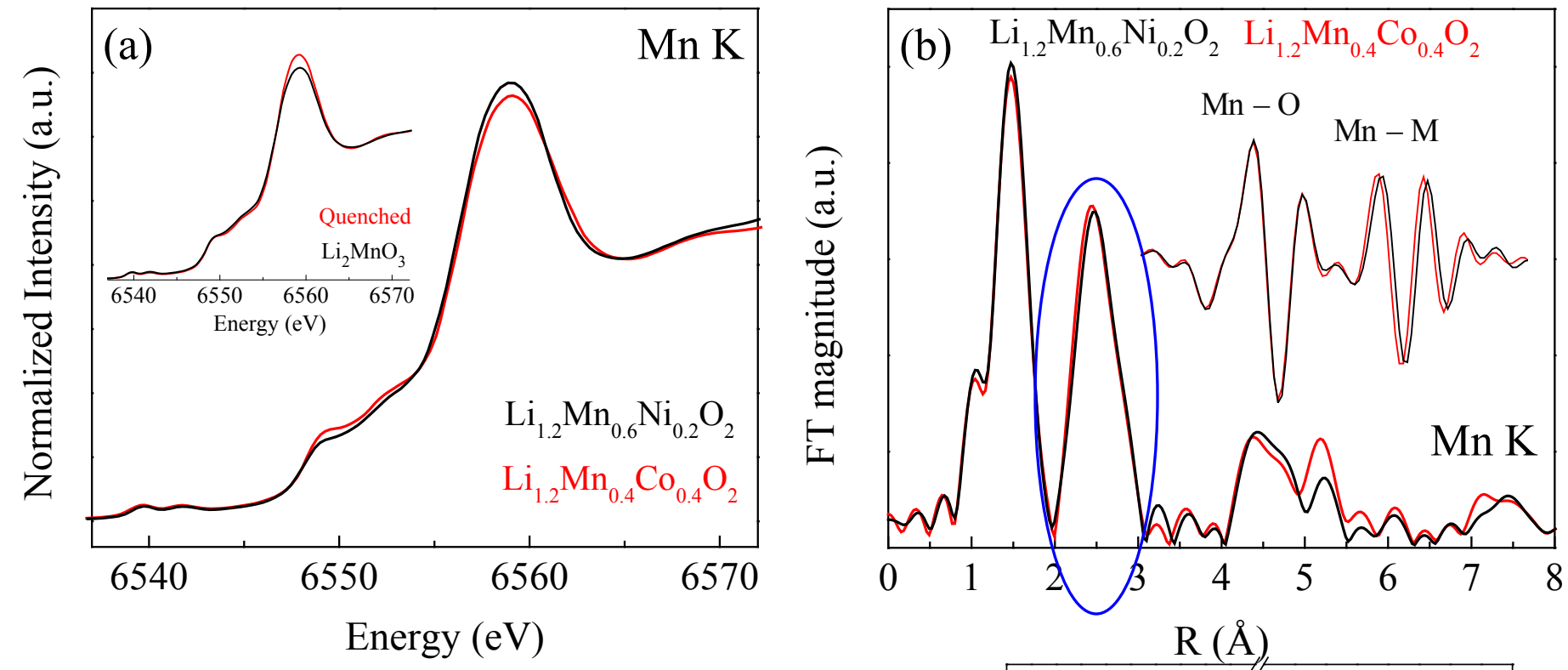


850°C for 12 hour followed by: Quenched – LN<sub>2</sub> cooled plates, Slow cooled – 16 hours to RT

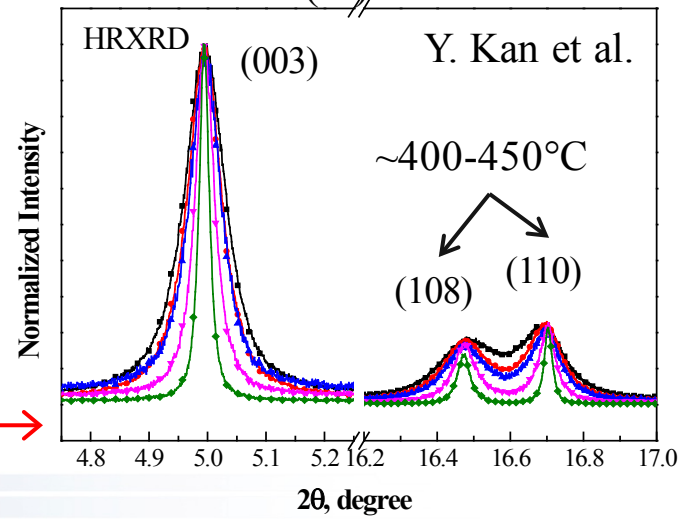


local “composite” structure persists regardless of cooling rates

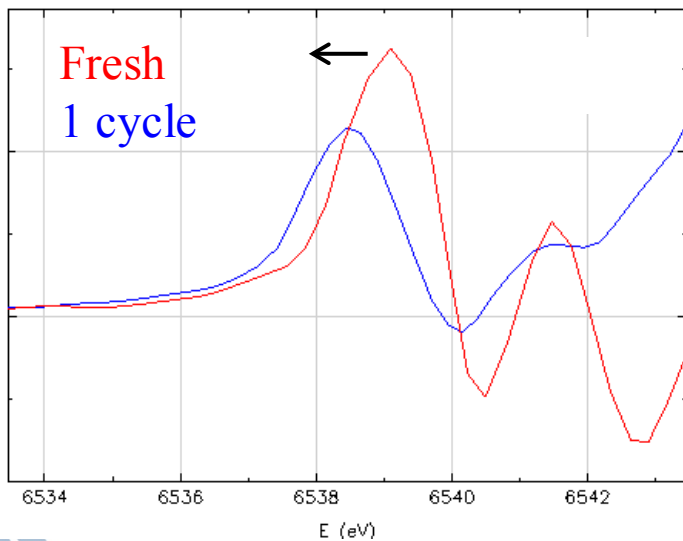
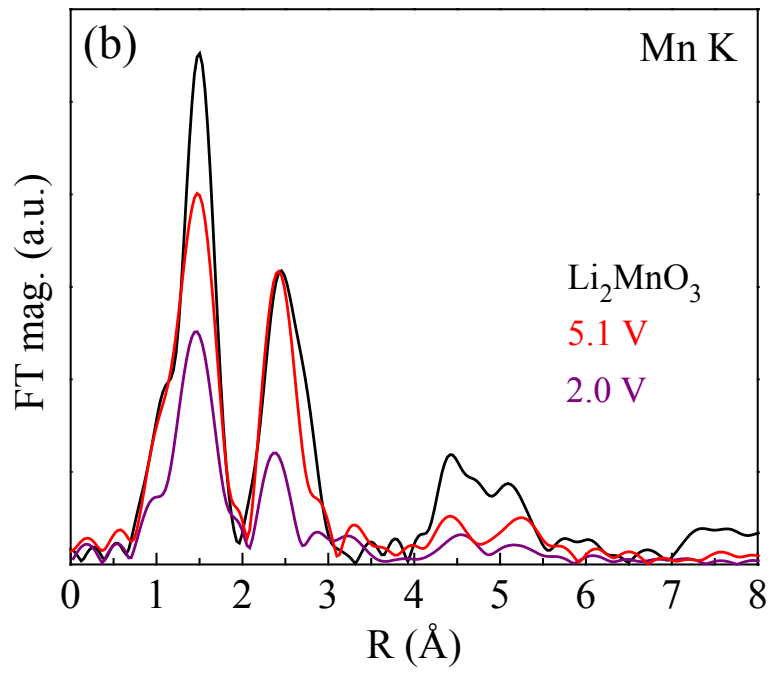
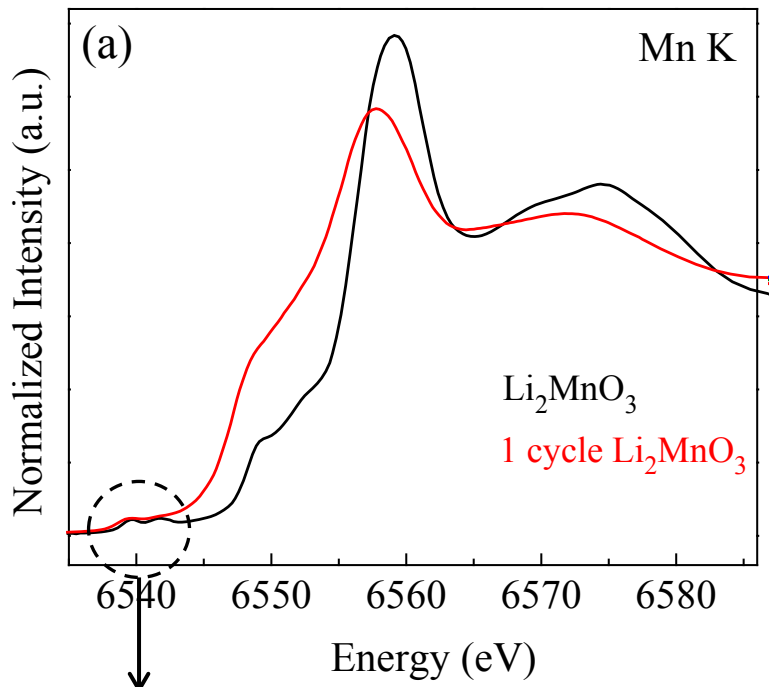




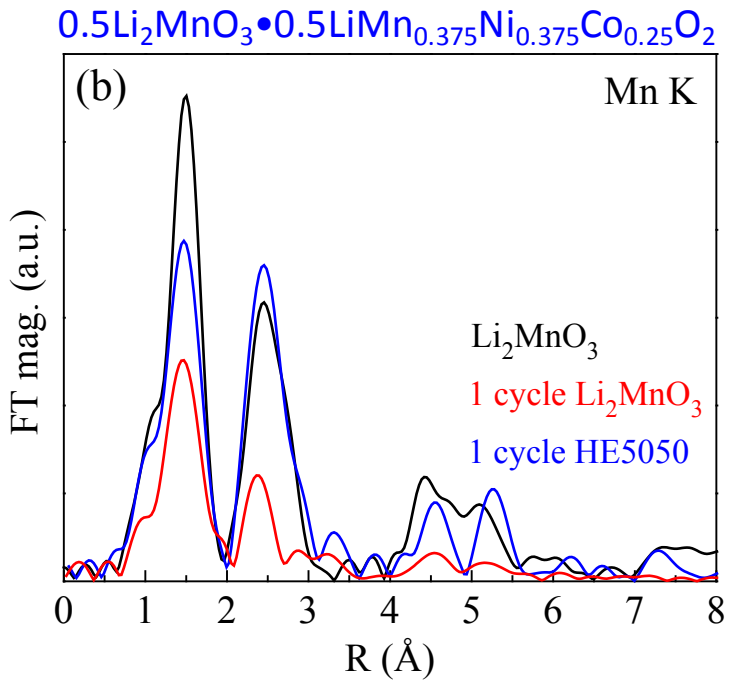
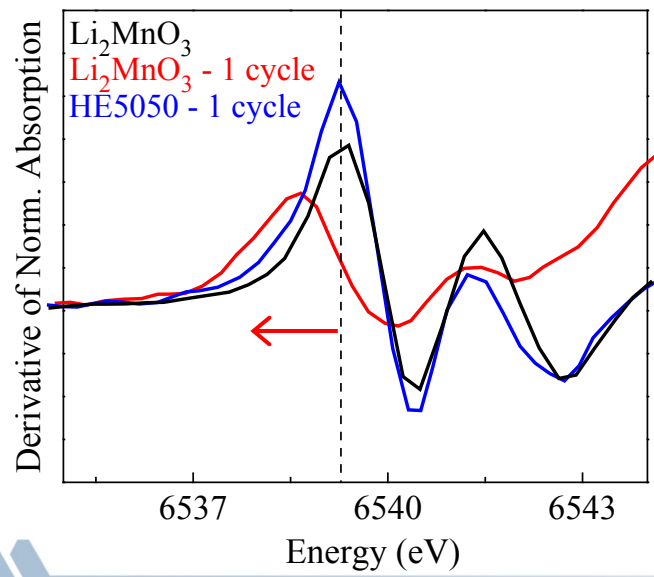
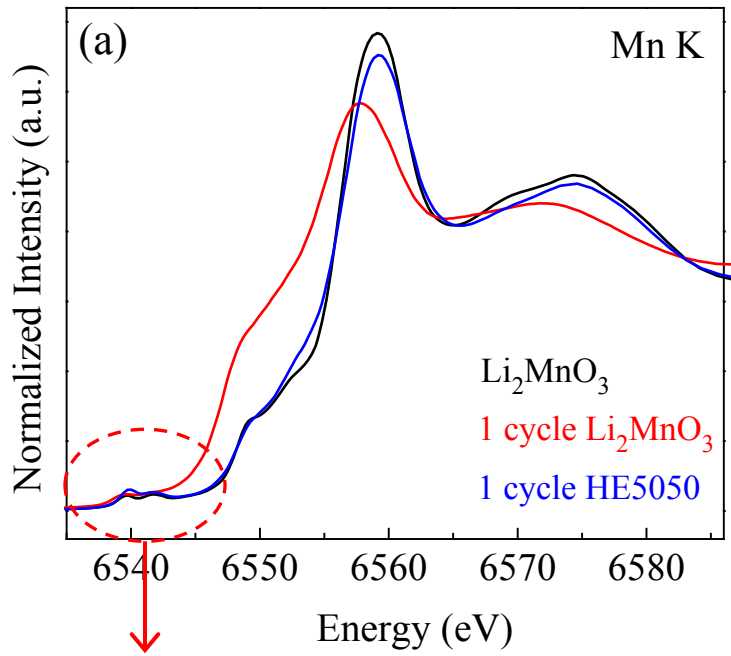
- Both samples quenched from 850°C
- Variations between compositions due to  $\text{Mn}^{4+}/\text{Ni}^{2+}$  interactions and  $\text{Li}^+/\text{Ni}^{2+}$  exchange
- **Li and Mn ordering dominates**, Mn-M CN  $\sim 4$  in both compositions regardless of cooling rates. **Related to the low-temp formation of  $\text{Li}_2\text{MnO}_3$ .** →



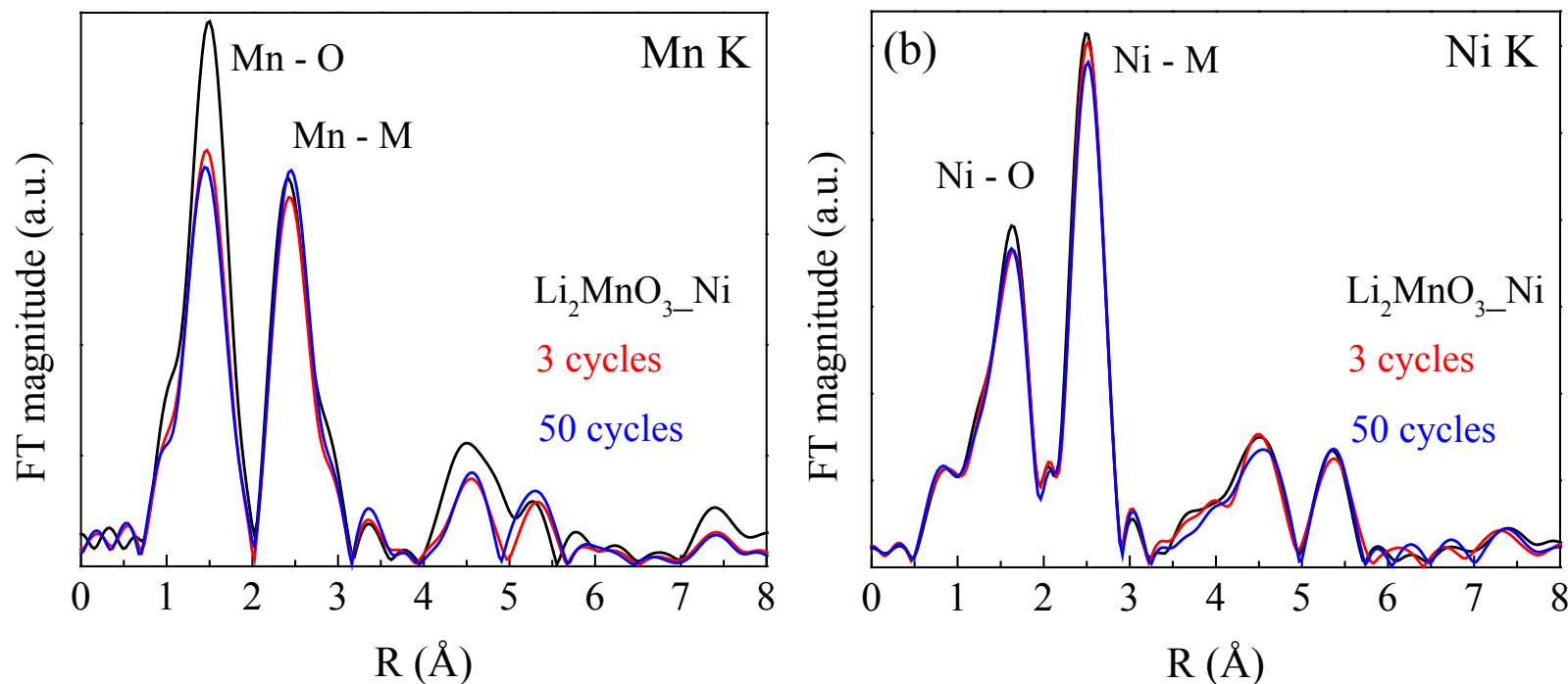




- **Mn<sup>3+</sup>** and extreme damping of EXAFS → **JT distortions**.
- Single O-bond gives Mn-O coordination ~3 (1.9 Å).
- JT distortion gives coordination of ~6 at (1.9/2.3 Å).
- Likely two phases present (Li<sub>2</sub>MnO<sub>3</sub>, ??).



- No evidence for significant Mn<sup>4+</sup> reduction to Mn<sup>3+</sup>
- Single O-bond gives Mn-O coordination of ~6 (1.9 Å) (See ES193, H. Iddir)
- No damping of Mn-M peaks
- Integrated LMO is clearly different than pure LMO

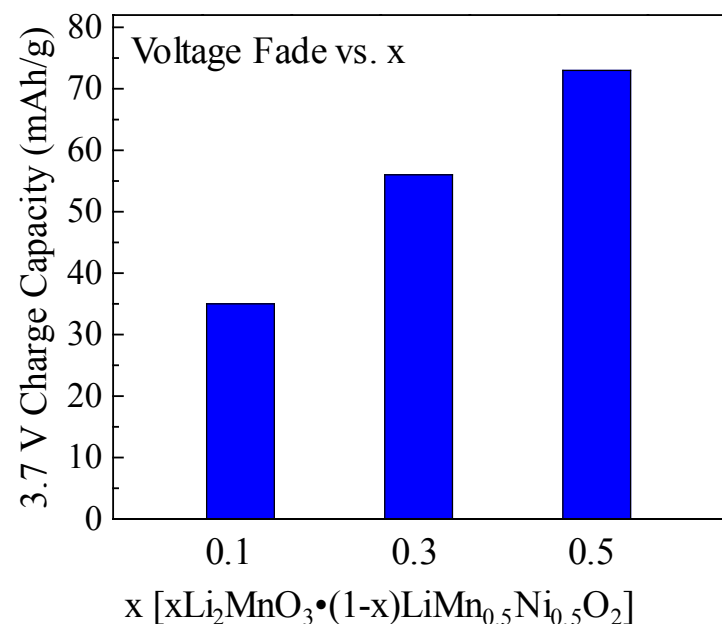
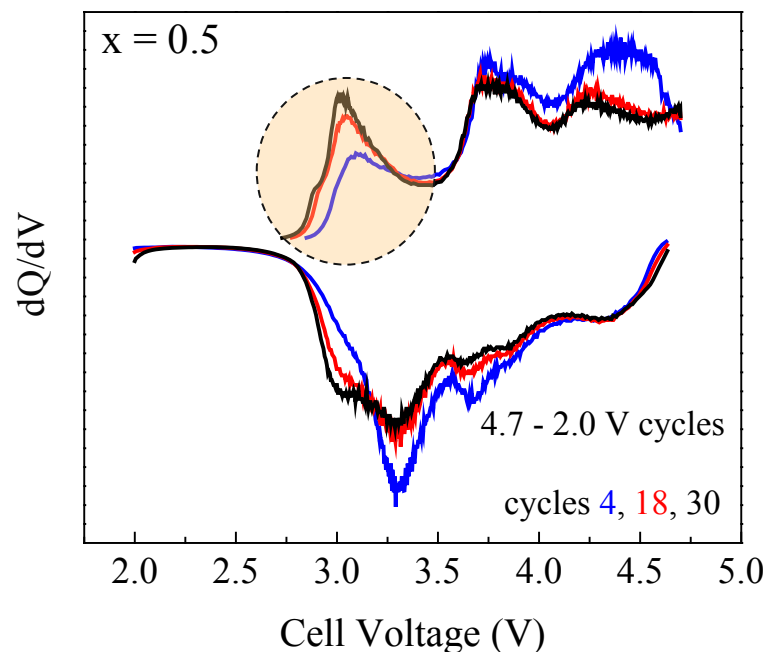


- Clear changes observed in the local manganese environment in early cycles.
- Very small changes to the nickel environment.
- Mn-Ni interactions in MnNi-rich regions stabilize Mn on edges of domains.
- Interior of Li/Mn-rich regions are most effected by cycling.

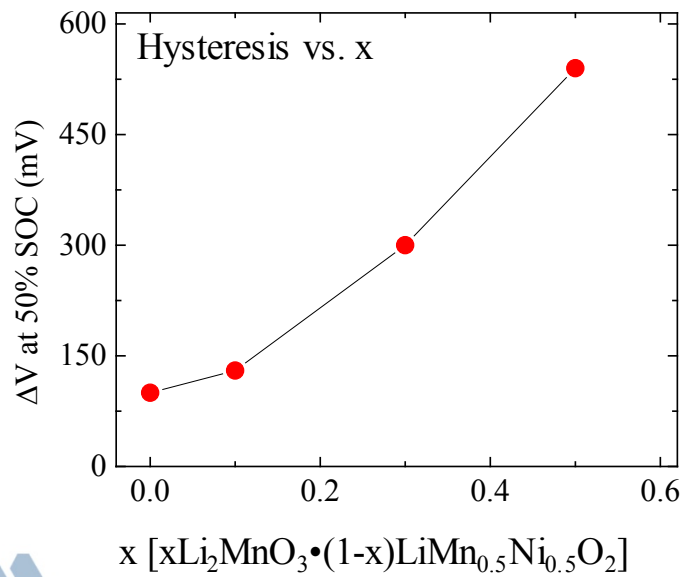
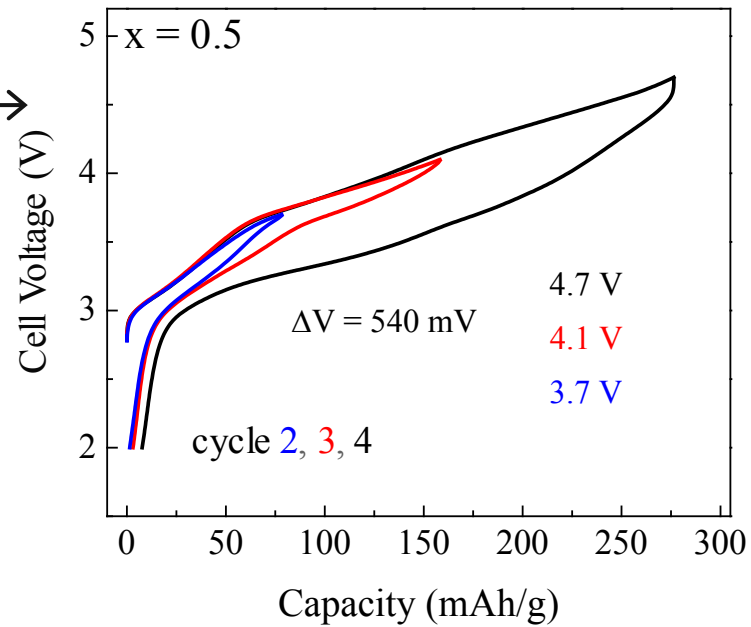
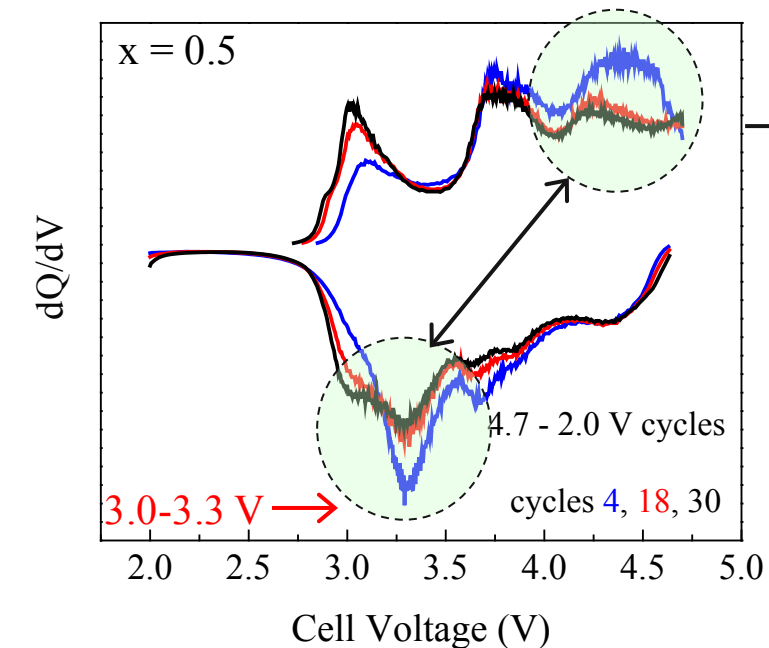
## Part 1 Summary

- Charge ordering, especially between Li and Mn, is the dominant factor dictating local, nanocomposite nature of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  oxides.
- Li/Mn rich domains form at low temperatures early in synthesis resulting in two different average environments for Mn relative to other TMs.
- Li/Mn rich domains are locally similar to  $\text{Li}_2\text{MnO}_3$  ; however, the observed electrochemistry is different than pure  $\text{Li}_2\text{MnO}_3$ .
- Li/Mn ordering plays a critical role in structural changes on cycling.



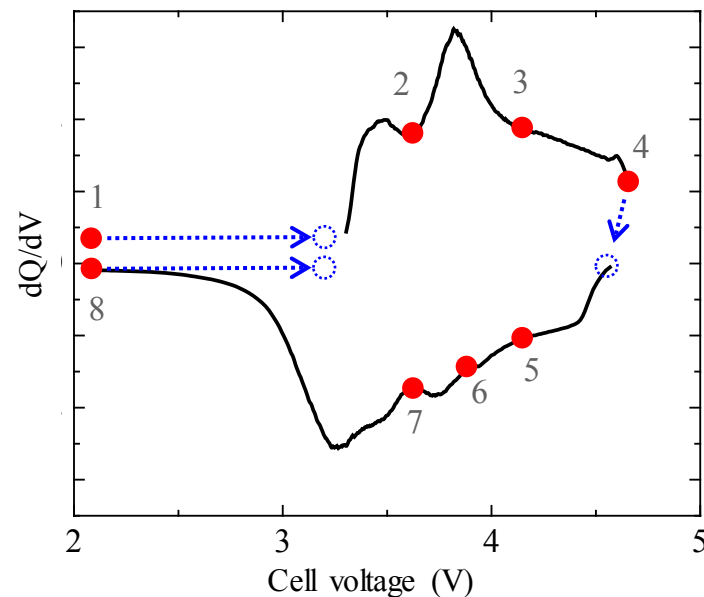
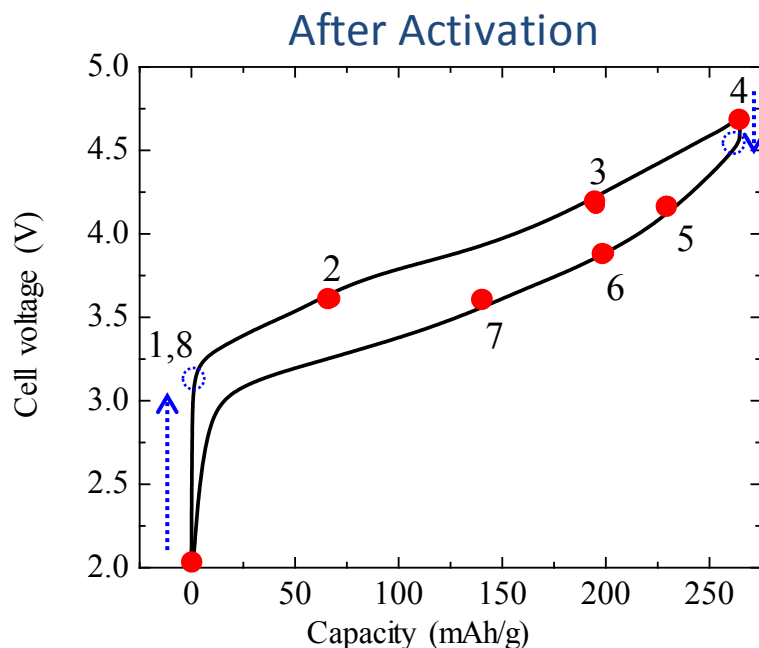


- Activation and high voltage cycling (~4.4 V) result in low voltage capacity (<3.5 V) due to structural changes – **VF configuration**.
- Magnitude of “VF capacity” is proportional to lithium in the transition metal layers of the initial composite – e.g., **Li and Mn ordering**.

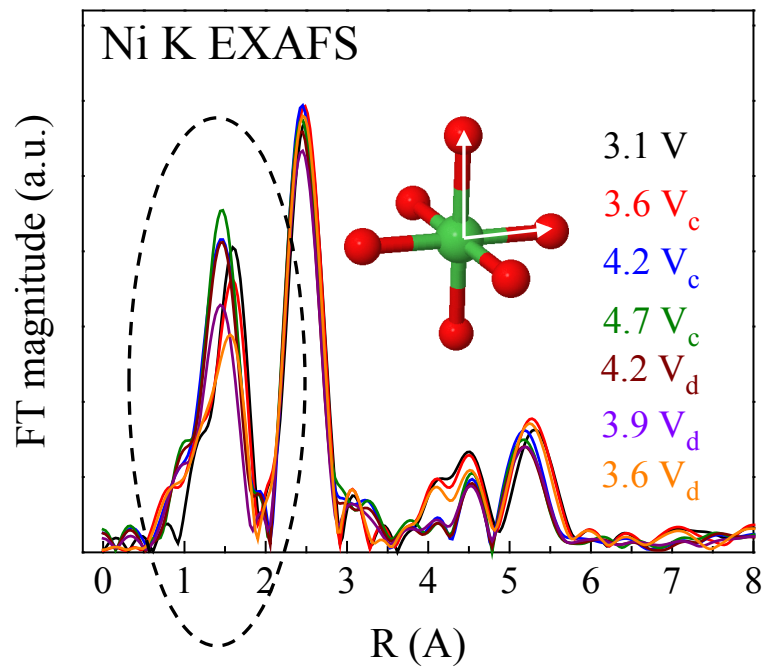
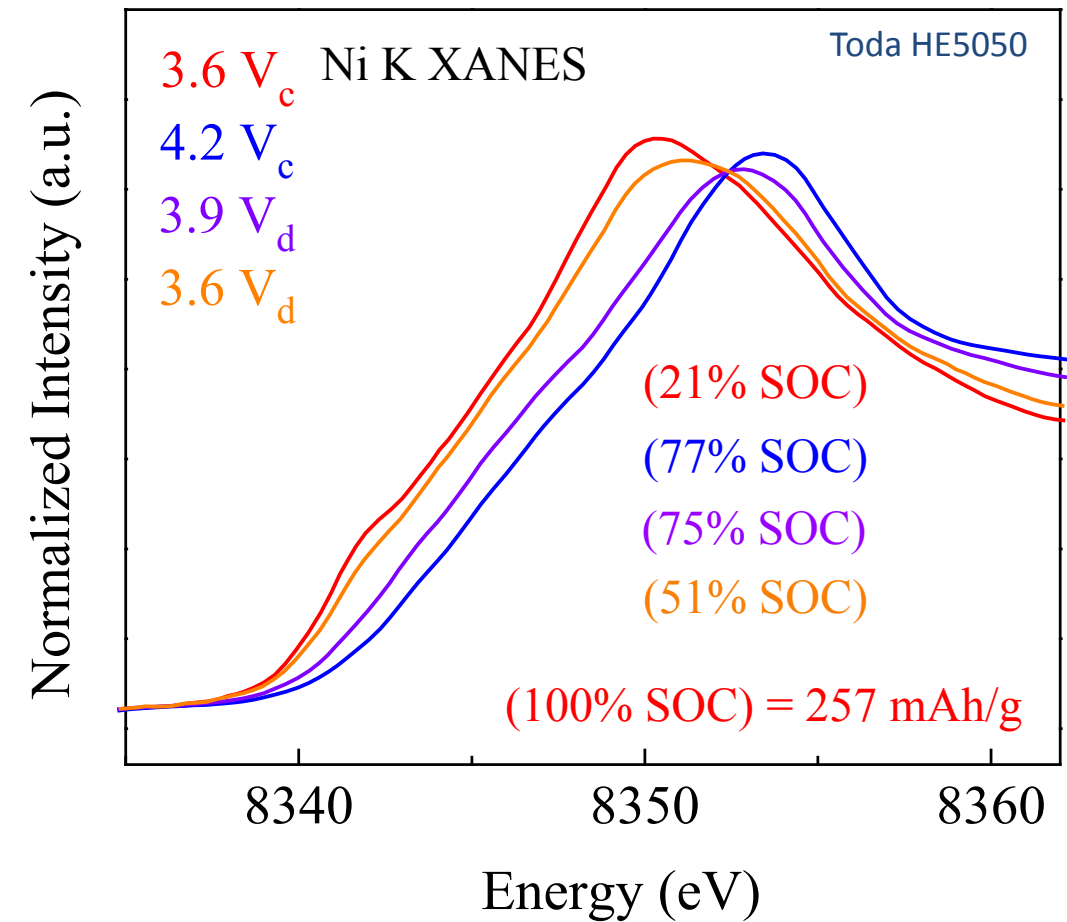


- Lithium removed above  $\sim 4.0 \text{ V}$  cannot be entirely re-accomodated until  $\sim 3.2 \text{ V}$  on discharge.
- Represents a  $\sim 1.0 \text{ V}$  hysteresis for some fraction of the overall lithium content.
- Magnitude depends on x in  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ .





- Study the structure and TM oxidation states at equivalent voltages and SOC's on charge and discharge (XAS and XRD) after activation.
- Charge/discharge to each point followed by 12 hour hold or rest.
- Cathodes were prepared and sealed in aluminized Mylar pouches under helium atmosphere for ex-situ XAS and XRD.

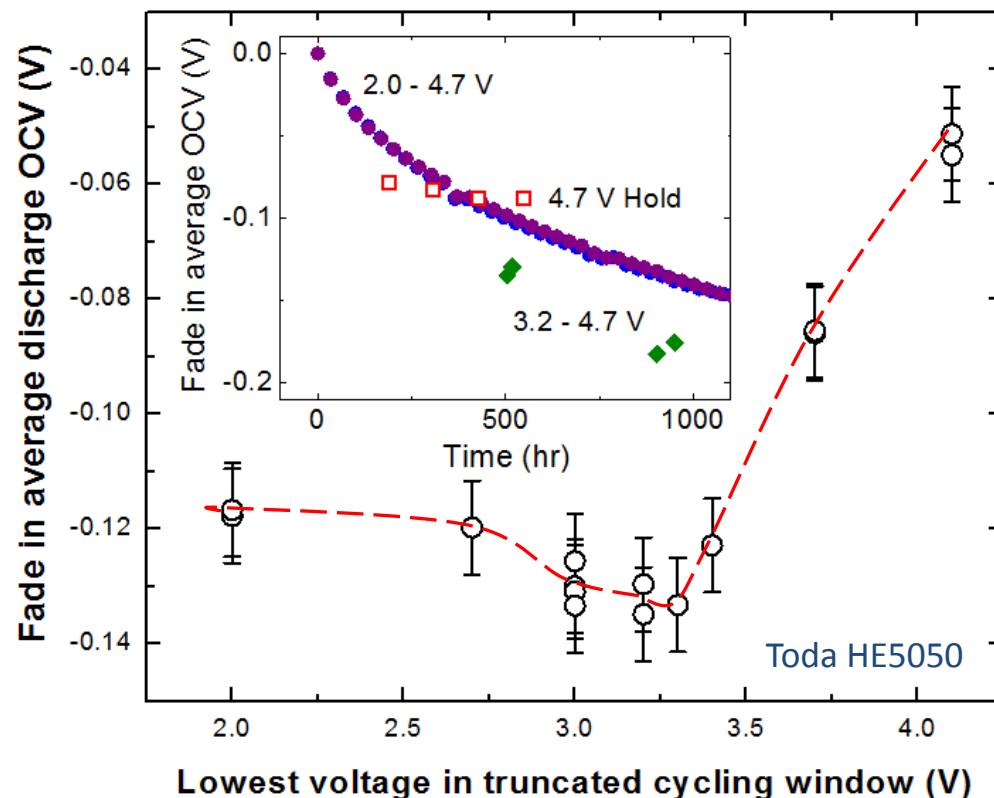


- Same trend for Mn and Co K-edge data → Spectroscopic evidence of hysteresis.
- Lithium does not have access to the same sites on charge and discharge even at equivalent lithium contents.



# VF and Hysteresis Are Correlated

Gallagher et al., *Electrochem. Comm.*, (2013)



- Cells cycled in truncated windows with decreasing, lower cutoff voltages (x axis).
- Upper cutoff voltage constant at 4.7 V.
- Main graph shows the average fade in discharge OCV between cycles 2 and 23 as a function of lower cutoff voltage (-----).
- Inset shows calendar time plot – Fade in OCV as a function of time on test – along with 4 cells held at 4.7 V for several, equivalent times on test (□).

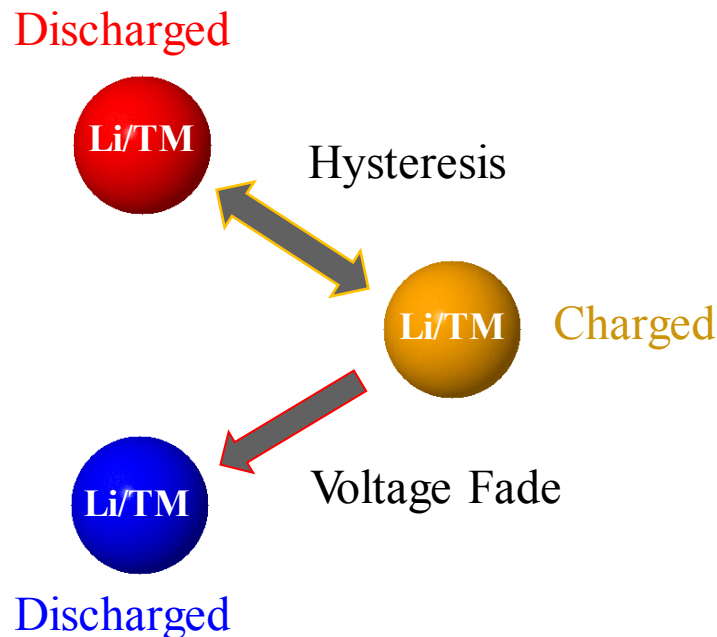
- Decreasing the lower cutoff voltage clearly increases voltage fade with a maximum fade found between 3.0 – 3.3 V.
- Cycling between 4.7 – 3.2 V accelerates voltage fade more than any other electrochemical exposure. Same window giving significant hysteresis.



# Proposed Mechanism of Voltage Fade and Hysteresis

- VF/hysteresis are related, structure and charge/discharge energetics differ.
- Any model for this class of materials must account for both.

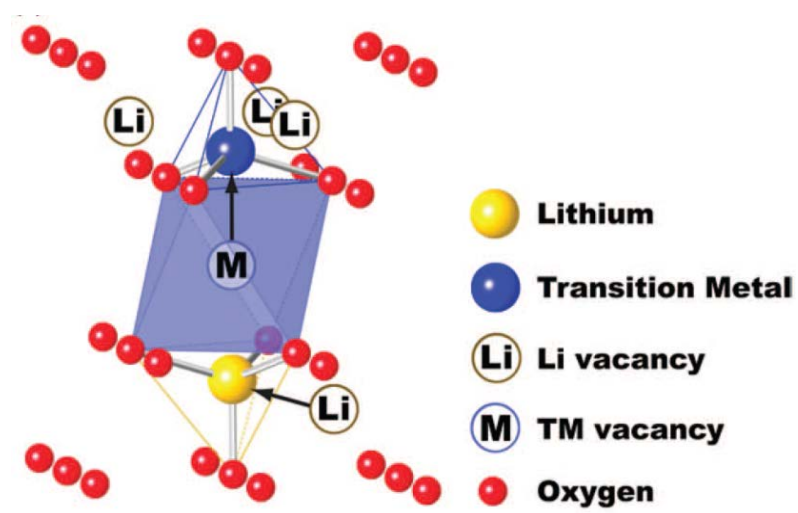
## Our Conceptual Interpretation of VF and Hysteresis



- Charging to  $\sim 3.8$  V and above induces migration to tetrahedral sites
- Cations are 'stuck' in that site until a critical Li content is reached on discharge ( $\sim 3.2$  V)
- At the critical lithium content cations can:
  - migrate back to original site (hysteresis)
  - continue on to the lithium layer (voltage fade)
  - remain 'stuck' – capacity loss, impedance rise

Gallagher et al., *Electrochem. Comm.*, (2013)

# Why Propose This Model?

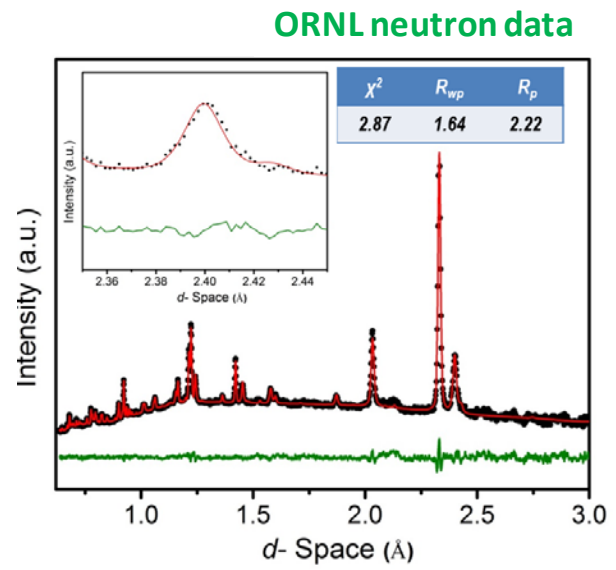
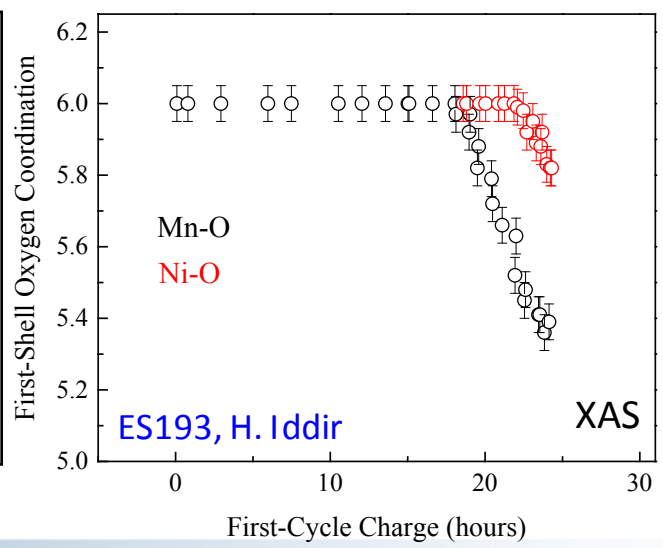
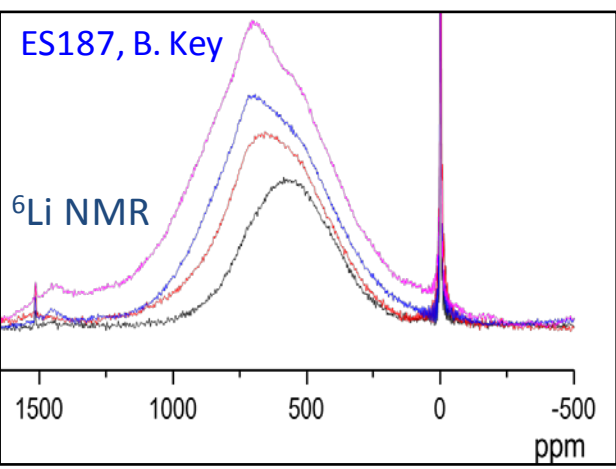


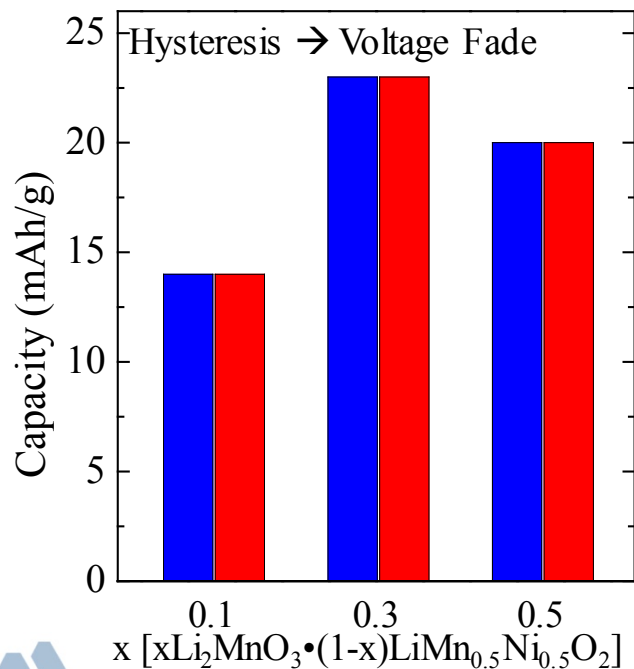
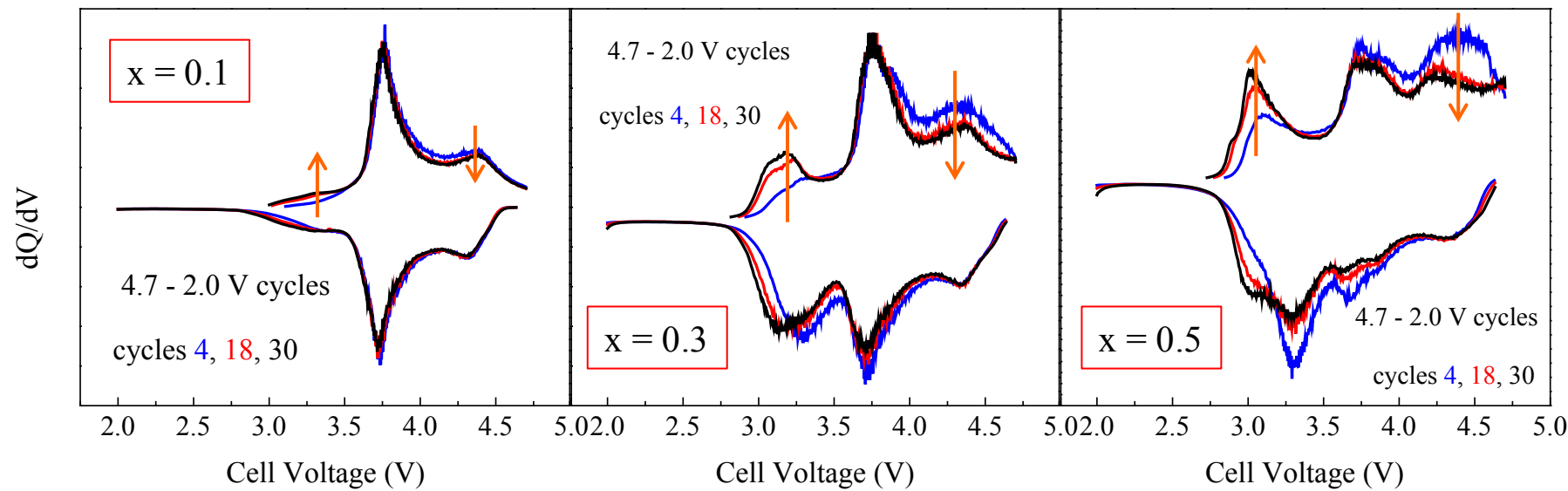
Ma et al., JES, 160 , A279 (2013)

- ‘Dumbbell’ formation (**tetrahedral migration**) in structural transformations of layered materials.

## Observed for other layered systems

- $\text{LiVO}_2$  (Thackeray)
- $\text{LiMnO}_2$  (Ceder, Bruce) 3.2 V processes
- $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$  (Balasubramanian)
- $\text{LiMn}_{0.5-x}\text{Cr}_{2x}\text{Ni}_{0.5-x}\text{O}_2$  (Karan)
- **Now have spectroscopic evidence for hysteresis mechanism (B. Key – ES187) (H. Iddir – ES193)**

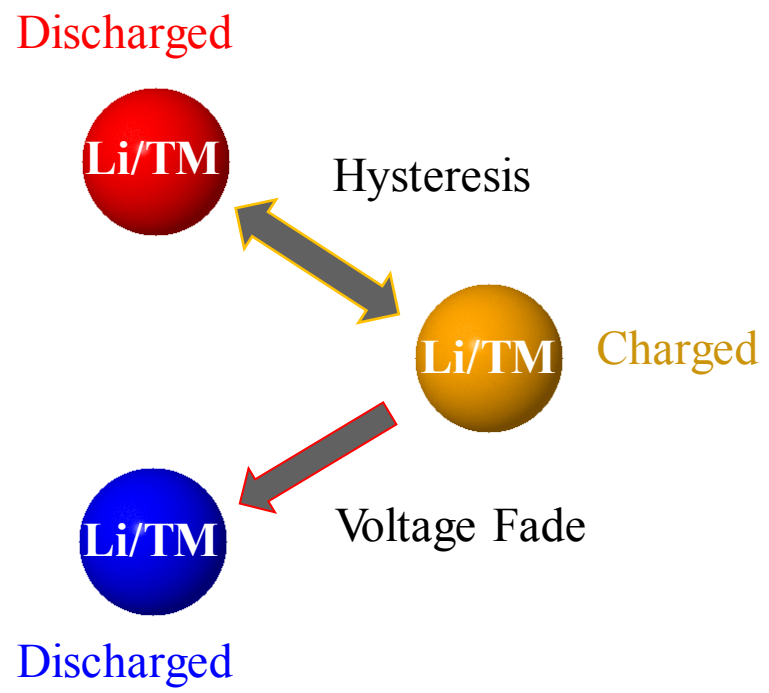
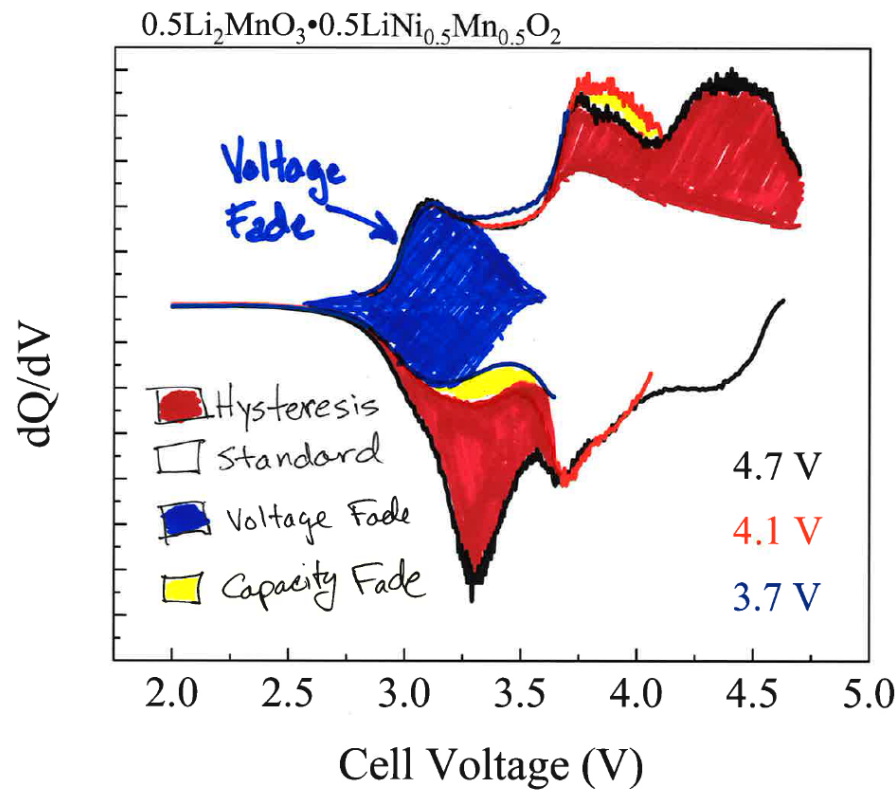




- Increase in capacity in 3.7 V region from cycle 4 to 30 (2.0 – 4.7 V windows) ‘Voltage Fade config.’
- Decrease in capacity in 3.8 – 4.7 V region from cycle 4 to 30 (minus irr. cap.) ‘Hysteresis config.’

Decrease in ‘hysteresis capacity’ leads to a concomitant increase in ‘voltage fade capacity’

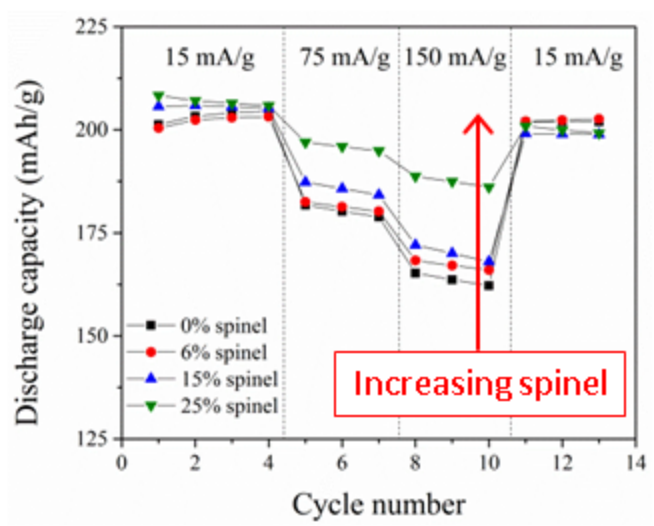
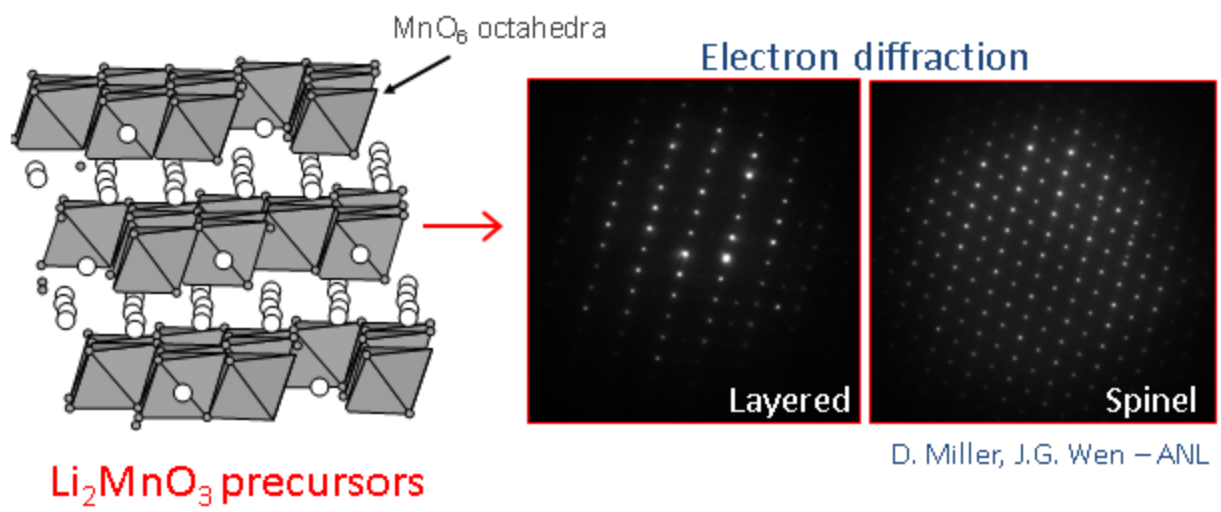
EC models agree – See ES189, D. Dees



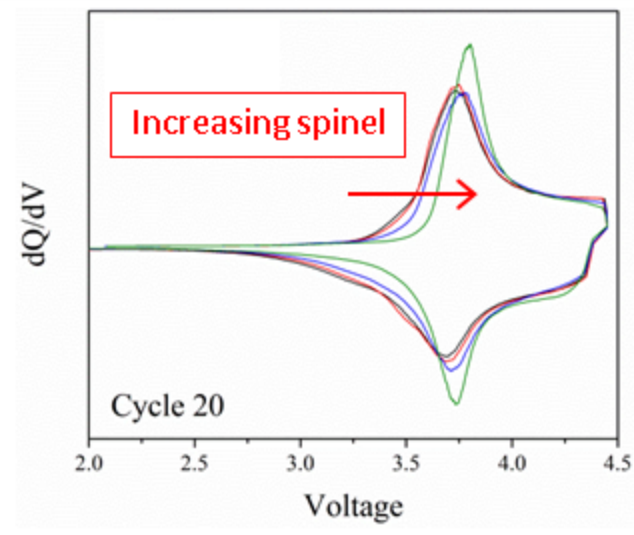
- Future studies will be aimed at direct verification, from experiment and theory, of cation occupancies (tetrahedral/octahedral) and oxidation states at different SOC.

# Exploring Stabilization of LMR-NMC Structures

- Different synthetic routes are being explored to produce layered-layered materials with a stabilizing spinel component (See BATT poster ES049). See Also C. Johnson ES190.



- Li<sub>2</sub>MnO<sub>3</sub> template used to integrate spinel component into layered composites.
- Similar strategy to stabilizing layered cathodes with integrated Li<sub>2</sub>MnO<sub>3</sub> component.
- Initial results show improved first-cycle efficiency and rate capability.



# Summary

- Charge ordering drives local “composite” nature of LMR-NMC materials.
- Voltage fade and hysteresis are related and depend on  $x$  in  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMnO}_2$ .
  - Activation of the  $\text{Li}_2\text{MnO}_3$  component is necessary for both
  - Both increase in prominence with increasing  $x$
  - Cycling above  $\sim 4$  V extracts lithium that is not accommodated on discharge until **3.0 – 3.3 V**
  - Window studies show that a lower cutoff of **3.0 – 3.3 V** accelerates Voltage fade faster than any other electrochemical exposure
- Proposed model involves tetrahedral migration of lithium and TMs on charge creating a barrier to lithium insertion until a sufficient driving force is established at some critical lithium content on discharge ( **$\sim 3.2$  V**).
- Driving force triggers one of three possibilities:
  - 1) TM/Li returns to its original octahedral position in the TM layer  $\rightarrow$  Hysteresis
  - 2) TM/Li migrates to a new octahedral position (e.g. in the Li layer)  $\rightarrow$  Voltage Fade
  - 3) TM/Li becomes trapped in the tetrahedral site  $\rightarrow$  Loss of capacity, increased impedance